

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.

THIS PAGE BLANK (USPTO)

(19)



Europäisches Patentamt

Eur pean Patent Office

Office européen des brev ts

(11)

Publication number:

0 060 622
A1

(12)

EUROPEAN PATENT APPLICATION

(21)

Application number: 82300749.7

(51)

Int. Cl.³: B 01 J 37/00, B 01 J 23/74,
C 01 C 1/04

(22)

Date of filing: 15.02.82

(30)

Priority: 18.03.81 GB 8108409

(71)

Applicant: IMPERIAL CHEMICAL INDUSTRIES PLC,
Imperial Chemical House Millbank, London SW1P 3JF
(GB)

(43)

Date of publication of application: 22.09.82
Bulletin 82/38

(72)

Inventor: Topham, Susan Ann, 43 Dunedin Avenue
Hartburn, Stockton-on-Tees Cleveland (GB)

(64)

Designated Contracting States: BE DE FR GB IT NL SE

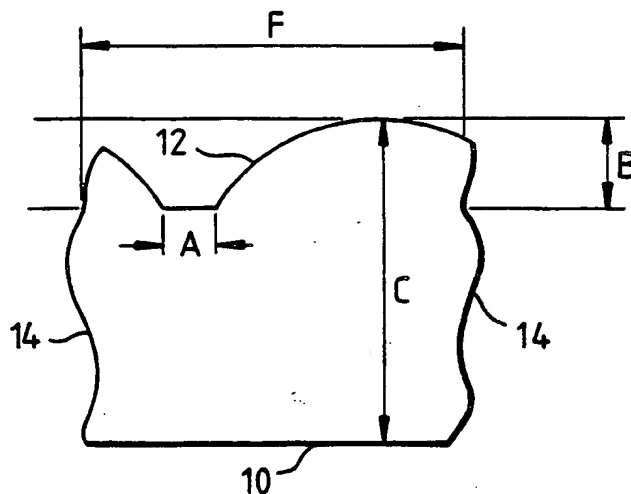
(74)

Representative: Chapman, Kenneth Hazel et al, Imperial
Chemical Industries PLC Legal Department: Patents
Thames House North Millbank, London SW1P 4QG (GB)

(54)

Catalyst.

(57) A metal oxide catalyst composition is in the form of particles having at least one face formed by solidification of melt in contact with a surface and preferably having at least one channelled surface whereby the pressure drop through a bed of such particles is limited. The particles are made preferably by casting a melt thinly and fracturing the resulting layer. Such a composition comprising iron oxide is a precursor of an ammonia synthesis catalyst.



EP 0 060 622 A1

Catalyst

This invention relates to a catalyst and in particular to a cast oxide composition convertible to a catalyst and a method of making it.

5 Certain catalysts, for example metallic iron catalysts to be used in ammonia synthesis, nitrile hydrogenation or carbon monoxide hydrogenation, are made by a method that includes melting iron oxide (usually mixed with small quantities of other oxides or oxide-precursors), allowing the melt to solidify, crush-
10 ing the solid and selecting particles of the required size range. This method is objectionable in that the crushing step produces much material of unwanted sizes, which has to be re-worked and is difficult to operate without producing a dusty environment. The particles in the required size range are irregular in shape and
15 thus do not fill a catalyst bed as uniformly as could be desired.

We have now devised a method capable of producing particles that are to a greater extent than before in wanted size ranges. The particles are of a shape not previously used in the catalyst art.

20 According to the invention a metal oxide catalyst composition is in the form of particles having at least one face formed by solidification of melt in contact with a surface.

Such particles preferably each also have one face formed by solidification not in contact with a surface. The remaining
25 faces are formed by fracture and these naturally are irregular.

The faces may be both substantially flat but, when the

particles are to be used in fluid contacting, at least one face formed by solidification is channelled. By this is meant that that face is so profiled that if it were placed in contact with a plane surface there would be formed at least one channel through which fluid could pass. As a result the pressure-drop through a bed of such particles is less than through a bed of particles having only flat faces formed by solidification. This is important when the particles are to be converted to catalyst to be used in a gas reaction at high pressure, for example ammonia synthesis, since excessive pressure-drop results in excessively high power consumption by the gas compressor and circulator.

The channelled profile can be based on any convenient surface shape, for example ribs, intersecting ribs, bosses, quilting or concentric corrugations. Any particle can have on its surface one or more than one channel-bounding projection. The percentage channel area of each particle, that is, the quotient
$$\frac{\text{projective cross-sectional area available for fluid flow}}{\text{total projective cross-sectional area}} \times 100$$
 of a rectangle having a height equal to the maximum particle depth and a length equal to the width of the particle in the plane beyond which it is not channelled, is preferably in the range 2 to 40, especially 6 - 25. The maximum channel depth preferably is in the range 10 - 70, especially 20 - 40%, of that of the whole particle.

The above-defined form is evidence of methods by which the particles can be made, namely by melting together the constituents of the oxide composition and/or precursors thereof and casting the melt on to a surface, the depth of the cast layer and the shape and pitch of any profiling and the rate of cooling being such that, on solidifying, the layer shrinks and separates from the surface, breaking the layer into particles possibly with light crushing but with under 50% ^w/_w formed by fracture other than through faces formed by solidification. It appears that casting thinly - to a depth of 1 - 20, especially 2 - 12 mm - on a surface introduces strains, as a result of which fracture takes place

readily and into particles having width between 0.25 and 4 times their depth and a relatively narrow size distribution. In particular few fines are formed and therefore the expensive remelting of the fines formed in considerable quantities with conventional crushing can be largely avoided. If desired the surface on which the melt is cast can be locally differentially cooled by differential thermal conduction, convection or radiation, to generate zones of weakness in the solid layer. The oxides after the casting are in the form of mutually adhering crystallites.

10 An alternative method, in which a profiled tool such as a roller is passed over the surface of the oxide mixture as it sets, also can produce the channelled shape and is a further feature of the invention. If desired, both methods can be used together and then the catalyst particles are channelled on both
15 sides.

By catalyst composition is meant one that is itself a catalyst or can be converted to a catalyst by chemical treatment or by addition of catalytically active material.

In an important form of the invention the oxide comprises
20 iron oxide, especially to the extent of at least 60% ^w/_w calculated as Fe_3O_4 on its constituents not volatile at 900°C. If the particles are to be converted to a hydrogenation catalyst for carbon monoxide or nitriles the particles typically contain at least 95% of iron oxide. If they are to be converted to an
25 ammonia synthesis catalyst, they will usually contain other oxides, of which the following are most typical (percentages ^w/_w):

	K_2O	0.3 to 2.0
	CaO	up to 5.0
	MgO	up to 2.0
30	Al_2O_3	0.5 to 5.0

These constituents are known as "promoters", and other promoters, such as oxides of rubidium, cesium, beryllium, lanthanides (especially cerium), actinides (especially uranium), molybdenum or tungsten, metals such as platinum group metals and minor constituents
35 such as silica, can be present instead of or in addition to the

typical promoters. In addition, such a catalyst can contain cobalt oxide suitably to the extent of 1 - 20% ^w/_w calculated as Co_3O_4 on the total precursor composition in which the iron oxide is assumed to be all Fe_3O_4 .

- 5 In other forms of the invention the oxide composition comprises one or more of the oxides of copper, nickel or cobalt and is then useful as a precursor of a catalyst for hydrogenation of carbon monoxide or nitriles. Other oxides that can be present alone or in addition include those of transition metals such as
- 10 those of Groups VA - VIIA of the Periodic Table and also of metals of Groups IIIA- IVA: in the latter event the oxide composition is a catalyst support, to which catalytically active material will be added.

After the steps of melting, casting and fracturing, the

15 following steps can be involved in converting the particles to catalyst:

- (a) classification, to remove the usually small quantity of fines and oversize and possibly to separate a plurality of wanted size ranges;
- 20 (b) tumbling, to remove sharp corners and edges and, in extreme cases, to produce approximately spherical particles;
- (c) reduction of reducible oxides to catalytically active metal;
- 25 (d) formation of catalytically active metal compound such as carbide or nitride;
- (e) passivation of such metal and/or compound by superficial oxidation;
- (f) addition of further constituents.

30 Preferably no further comminution or agglomeration is carried out.

Of these, steps a and c are almost always necessary.

Step e, carried out by the catalyst manufacturer, and followed by a further application of step c by the catalyst user after charging a reactor, is important in the ammonia industry, since it

35 enables the synthesis operator to start the process up more quickly.

Step f, an example of which is impregnation by a rare earth salt solution, can be applied at any stage, preferably after reduction, and is recommended by some catalyst manufacturers.

5 The invention includes also a metal composition formed from the oxide composition by reduction, a passivated composition formed from the metal composition by superficial oxidation and a metal composition formed from the passivated composition by reduction. Either of such metal compositions is a catalyst for hydrogenation.

10 There is provided also hydrogenation processes using such a catalyst, in particular an ammonia synthesis process over a metallic iron catalyst in any known conditions, that is, in the pressure range 20 - 500 bar abs. and a temperature in the range 250 - 550°C. Because of the low pressure drop and high activity
15 the catalyst is suitable for recently developed processes at under 200 bar abs. pressure, especially for the new low-energy processes at pressures in the range 30 - 120 bar abs. and at relatively low temperatures such as 350 - 450°, so as to obtain a more favourable equilibrium.

20 The invention is illustrated by the accompanying drawing, in which

Figure 1 shows a projective elevation of a particle according to the invention; and

25 Figure 2 shows in sectional elevation part of a casting tray in which the particles can be made.

In figure 1 the particle has a substantially flat face 10, which was the upper surface formed on solidification of a melt, a profiled face 12 formed by solidification of the melt in contact with a surface, and faces 14 formed by fragmentation. Profiled
30 face 12 includes parts of domed regions of height B, separated at their bases by a distance A. The total width of the particle at the plane of the base of the domed regions is F, and thus the rectangle by which the channel area of the particle is to be defined has the area FC. The total height C of the particle is of
35 the same order as width F, but F can be controlled in ways to be

described below.

In figure 2, casting tray 20 is formed on its internal underside with lengthwise corrugations separated by distance A and of depth B, width D and cross-sectional radius E. In use, 5 tray 20 is normally filled to level 22, giving depth C. When a trayful of melt is cooled and the resulting layer separated and lightly crushed, fracture takes place along lines parallel with and transverse to the corrugations and the size F of the fragments is controlled by reference to depth C and the cooling rate, for a 10 given tray profile and oxide composition: thus for making relatively small particles the depth of melt above A would be smaller in proportion, to ensure fracture between domed regions.

EXAMPLE

A finely powdered mixture of recycled undersize product, 15 natural Swedish magnetite, calcium carbonate, alumina and potassium carbonate corresponding to the composition % w/w:

	Al_2O_3	2.4
	CaO	1.4
	K_2O	1.0
20	SiO_2	0.4
	Fe_3O_4	balance

was melted in an electric furnace for 30 minutes at about 1600°C and then poured out into mild steel casting trays having a bottom profile as shown in the accompanying drawing, the dimensions de- 25 noted by letters being as follows, mm:

	A	1
	B	2
	C	7
	D	7
30	E	4
	F	7

The mixture was allowed to cool in ambient air: on solidifying it shrank and ceased to adhere to the tray. The resulting layer, partly broken, was lightly crushed on a vibrat- 35 ing sifter having an upper 9.5 mm sieve and a lower 5 mm sieve.

Particles held on the 9.5 mm sieve were crushed and returned to the sifter. Particles passing the 5 mm sieve were returned to a reservoir, to be used in a later melt: in industrial practice they would be further sieved to give a 3 to 5 mm fraction suitable for radial-flow ammonia synthesis reactors and a fines fraction to be used in a later melt. Particles in the size range 3 to 9.5 mm had one flat face and a corrugated face opposite the flat face and constituted preferred compositions according to the invention. They had the following physical and chemical properties

10	Crystallite size	about 100 nm
	True density g cm^{-3}	4.83
	particle density g cm^{-3}	4.79
	pore volume $\text{cm}^3 \text{g}^{-1}$	0.002
	Fe^3/Fe^2 by atoms	2.42
15	size analysis % w/w over 9.5 mm	12.6 (separated)
	8 to 9.5 mm	38.5
	6.35 to 8 mm	36.3
	4.75 to 6.35 mm	11.8
	3.35 to 4.75 mm	0.8
20	mean particle diameter 7.95 mm (standard deviation 1.4 mm)	
	percentage channel area 8.6 - 11.4 (30 - 40% of rectangle FB)	

These properties are substantially equal to those of a commercially available ammonia synthesis catalyst made by crushing and classifying; however, the weight percentage of undersize and oversize material was only 25, compared with a typical 90 for the conventional method, on a once-through basis. Very little dust was produced. The particle crush strength and the pressure drop exerted on flowing gas were also measured and were found to be substantially equal to those of the commercial catalyst.

30 Test in ammonia synthesis

A sample of particles (20 g) was diluted with silica chips (80 ml), charged to a semi-technical reactor and over it was passed at 100 l h^{-1} (calculated to 24°C , 1 atm) a pure 3:1 hydrogen:nitrogen mixture at 50 atm pressure. The temperature was raised rapidly to 350°C , then by 15°C at hourly intervals up to

475°C, and held at 475°C overnight and until no further increase in outlet gas ammonia concentration took place, showing that reduction was complete.

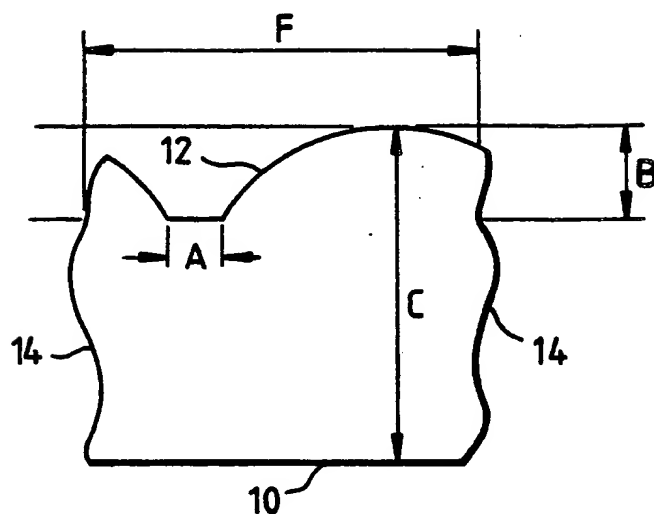
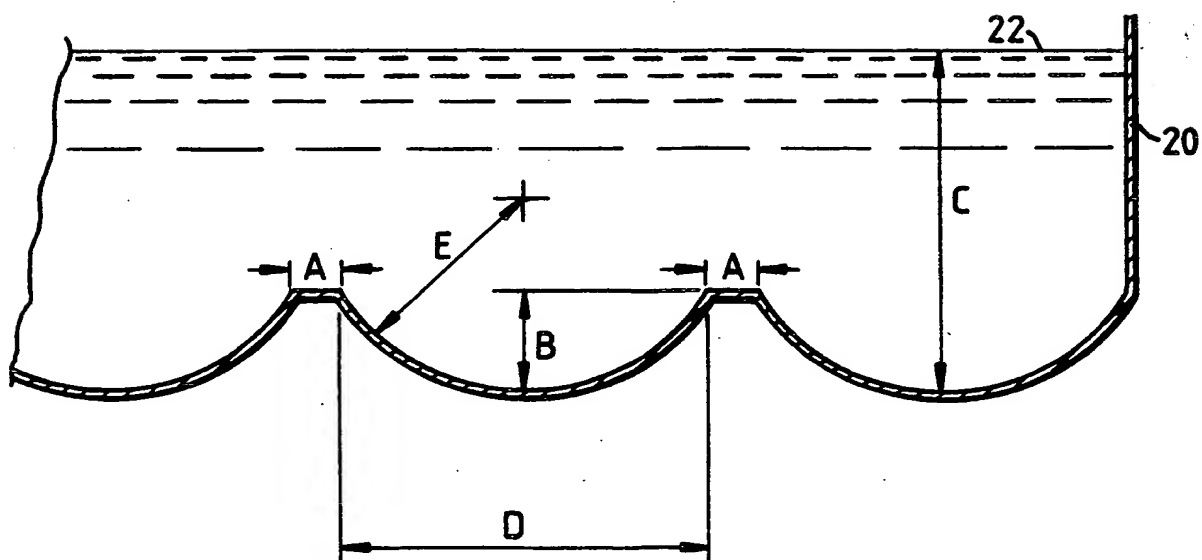
The temperature was adjusted to 450°C and the gas flow rate adjusted to various levels over a range to give steadily about 14% conversion to ammonia, then 13, then 12%, whereafter the results were represented as a graph of percentage conversion against flow rate per gram of catalyst. Then to simulate catalyst ageing during long term use the temperature was raised to 550°, held there for 255 hours and lowered to 450°C. A second activity test by flow rate adjustment was then carried out. A similar set of tests were applied to a commercially available catalyst in a parallel reactor. The flow rates, calculated to 1 g of catalyst, and the relative activities of the two catalysts are shown in the Table.

TABLE

Catalyst condition	% conv.	Flow rates l h ⁻¹ g ⁻¹		Relative activity	
		Commercial	Invention	Commercial	Invention
Fresh	14	2.77	2.95	100	107
	13	3.35	3.55	100	106
	12	4.17	4.45	100	107
Aged	14	2.37	2.60	86	94
	13	2.97	3.18	89	95
	12	3.53	3.70	85	88

PA/KHC/MP
4 February 1982.

1. A metal oxide catalyst composition in the form of particles having at least one face formed by solidification of melt in contact with a surface.
2. A composition according to claim 1 in the form of particles having also one face formed by solidification of melt not in contact with a surface.
3. A composition according to claim 1 or claim 2 in the form of particles in which at least one face formed by solidification is channelled.
4. A composition according to claim 3 in which the percentage channel area of the particles is in the range 6 - 25.
5. A composition according to any one of the preceding claims comprising iron oxide to the extent of at least 60% ^{w/w} calculated as Fe_3O_4 on its constituents not volatile at 900°C.
6. A composition according to claim 5 and containing one or more ammonia synthesis catalyst promoter oxides and/or cobalt oxide.
7. A method of making a composition according to any one of the preceding claims which comprises melting together the constituents of the oxide composition and/or precursors thereof, casting the melt thinly on a surface, the depth of the cast layer and the shape and pitch of any profiling and the rate of cooling being such that, on solidifying, the layer shrinks and separates from the surface and breaking the layer into particles with under 50% ^{w/w} formed by fracture other than through faces formed by solidification.
8. A catalyst comprising metallic iron and made by reducing a composition containing iron oxide according to any one of claims 1 to 6 or produced by the method according to claim 7.
9. An ammonia synthesis process over a catalyst according to claim 8.
10. An ammonia synthesis process according to claim 9 and carried out at a pressure in the range 30 - 120 bar abs. and a temperature in the range 350 - 450°C.

Fig.1.*Fig.2.*



European Patent
Office

EUROPEAN SEARCH REPORT

0060622
Application number

EP 82 30 0749

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X,Y	DE-C- 476 380 (SOCIETE AIR LIQUIDE) * page 2, lines 7-72 *	1,2,5-10	B 01 J 37/00 B 01 J 23/74 C 01 C 1/04
Y	US-A-3 644 216 (ROGER EGALON et al.) * column 3, lines 1-71 *	1,2,5,7-10	
Y	FR-A- 812 290 (I.G. FARBEN INDUSTRIE A.G.) * page 1, line 59 - page 2, line 18; claim 3 *	6	
A	GB-A- 833 878 (OSTERREICHISCHE STICKSTOFFWERKE)		
A	STAHLEISEN-SCHRIFTEN, vol.3, 1952, Dusseldorf (DE), K. MAYER: "Was der Siemens-Martin-Stahlwerker von seiner Arbeit wissen Muss", pages 142-144 * page 143, lines 5-12; page 144, figure 215 *	1	TECHNICAL FIELDS SEARCHED (Int. Cl. 3) B 01 J 23/00 B 01 J 35/00 B 01 J 37/00 C 01 C 1/00
Y	GB-A- 227 491 (LUIGI CASALE) * claims 1,3 *	6	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 09-06-1982	Examiner HOFFER H.R.P.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO Form 1503, 03/82